JAPANESE KOKAI PATENT (A), HEI 10-324056
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TITLE OF INVENTION : Inkjet Recording Material and the Production Method Thereof

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NUMBER OF CLAIMS : 5

REQUEST FOR EXAMINATION : None

[Abstract]
[Object] To provide an inkjet recording material having excellent water resistance.

[Solution] An inkjet recording material having an ink-accepting layer provided on the hydrophobic supporting member, where the ink-accepting layer is formed by coating and drying a coating fluid containing a polyvinylacetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains a cationic substance and synthetic amorphous silica, on the hydrophobic supporting member.

Claims

[Claim 1] An inkjet recording material having an ink-accepting layer on a hydrophobic supporting member, where the ink-accepting layer is formed by coating and drying a coating fluid containing polyvinyl acetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains a cationic substance and synthetic amorphous silica, on the hydrophobic supporting member.

[Claim 2] The inkjet recording material according to Claim 1, where the ink-accepting layer contains a coloring pigment.

[Claim 3] The inkjet recording material according to Claim 1, where the thickness of ink-accepting layer is 30 – 80 μm.

[Claim 4] Production method of inkjet recording material having an ink-accepting layer on a hydrophobic supporting member, as characterized by coating a coating fluid comprising polyvinylacetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains a cationic substance and synthetic amorphous silica on a hydrophobic supporting member, and subsequently drying it to form the ink-accepting layer.

[Claim 5] The production method of inkjet recording material according to Claim 4, where the coating fluid contains a coloring pigment.

Comprehensive explanation of invention

[0001]

[Technological field of invention]

This invention relates to a recording material for an inkjet printer that ejects minute liquid droplets such as aqueous ink droplets containing color substance such as dye or pigment through its nozzle to print a monochromic or full color image at high speed. More particularly, this invention relates to a recording material that has excellent water resistance.

[0002]

[Prior art]

Because the ink-accepting layer of inkjet recording material must be able to absorb a large amount of aqueous ink, hydrophilic and/or water-absorbing binder has been used traditionally as the binder in such ink-accepting layer. For example, polyvinyl alcohols and its derivatives, polyvinyl pyrrolidone, polyvinyl acetals, oxidized starch, esterified starch, carboxymethylcellulose, hydroxyethylcellulose and so on have been used as such binder. Even though the ink-absorbing layer that employs such binders can absorb a large amount of water-based ink, it tends to have an extremely poor resistance against water. Thus, if water such as rain adhered on such layer, the ink-accepting layer may drop off or the ink in the printed area may run and be lost. To solve these problems, Japanese Patent [illegible] discloses an inkjet recording material that has an ink-accepting layer made of fine silicic acid particles, emulsion polymer and cataionic

polymer coated on the supporting member. In this Japanese Patent, water is used as the solvent of the coating fluid to form the ink-accepting layer, but this ink-accepting layer does not have sufficient water resistance.

[0003]

And, Japanese Kokai Patent HEI 8-25841 (1995) discloses an inkjet recording material in which is formed an ink-accepting layer that contains a hydrophobic resin and pigment on at least one side of the supporting member. And, Japanese Kokai Patent HEI 8-230174 (1995) discloses a coated sheet that has an ink-absorbing layer made of binder and pigment on at least one side of the substrate film, in which the solvent to be used for coating the absorbing layer is made of a mixture of a good solvent and a poor solvent to the binder, boiling point of the good solvent is lower than the boiling point of the poor solvent, and density of the absorbing layer is no higher than 1.0 g/cm^3. In this patent, a thermoplastic polyester resin is described as the binder to be used in this coated sheet. According to the inkjet recording material disclosed in that Japanese Kokai Patent, some degree of improvement in water resistance can be achieved. Inks with excellent water resistance such as pigment ink or water-resistant dye ink and so on are used as the aqueous ink for use in the inkjet printers in recent years. Therefore, there is a demand for the inkjet recording material that has improved enough water resistance and can be used for such types of inks.

[0004]

[Problems to be solved by invention]

Therefore, the object of this invention is to provide an inkjet recording material with excellent water resistance and its production method.

[0005]

[Means to solve the problems]

As a result of an extensive investigation, the present inventor has discovered that the above-said object can be met by the inkjet recording material that has an ink-accepting layer made from a coating fluid that contains a polyvinyl acetate resin having a specific degree of polymerization and organic solvent that contains cationic substance and synthetic amorphous silica. This invention was made based on this discovery. Thus, this invention intends to provide an inkjet recording material having an ink-accepting layer on a hydrophobic supporting member, where the ink-accepting layer is formed by coating and drying a coating fluid comprising polyvinyl acetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains a cationic substance and synthetic amorphous silica, on a hydrophobic supporting member. And, this invention provides also a production method for the inkjet recording material that has an ink-accepting layer provided on a hydrophobic supporting member, as characterized by coating and drying a coating fluid comprising polyvinyl acetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains a cationic substance and synthetic amorphous silica, on a hydrophobic supporting member, to form the ink-accepting layer.

[0006]
[Form of practice of invention]
Inkjet recording material of this invention is explained comprehensively first in the following. Examples of the hydrophobic supporting member to be used in this invention are polyethylene terephthalete, polypropylenes, polyvinylchlorides or their foamed films; the films that contain pigment such as calcium carbonate or titanium oxide or pearl pigment in such polymer films; the films made of polyesters, polystyrene, polyvinylchlorides, polymethyl methacrylates, polyethylenes or polycarbonates; light-blocking (or opaque) hydrophobic supporting members such as white synthetic papers, white polyester films and so on. Among them, preferred examples are opaque hydrophobic supporting members such as white synthetic paper and white polyester films. And, an undercoat layer to improve bondability of the film with the ink-acceptting layer or the film that has been treated with corona discharge may be used also. Thickness of the hydrophobic supporting member is 25 – 500 μ, preferably 50 – 130 μm.

[0007]
The ink-accepting layer to be provided on the hydrophobic supporting member of the inkjet recording material of this invention is explained next in the following. The ink-accepting layer is formed by coating and drying the coating fluid made of polyvinyl acetate resin having a degree of polymerization 1000 – 10,000, and an organic solvent that contains cationic substance and synthetic amorphous silica, on the hydrophobic supporting member. Examples of the organic solvent to be included in the coating fluid are methanol, ethanol, acetone, methylethyl ketone, benzene, toluene, methylcellosolve, ethylcellosolve, methylcellosolve acetate, methyl acetate, ethyl acetate, isobutyl acetate, amyl acetate, cyclohexanone, diacetone alcohol, butylcellosolve, 2-ethyl hexanol, diethyleneglycol monoethyl alcohol, N-methyl pyrrolidone, γ-butyrolactone, or dimethylacetamide and so on. Content of the organic solvent in the coating fluid is 55 – 95 weight %, preferably 60 – 90 weight %. And, polyvinyl acetate resins having a degree of polymerization 1000 – 10,000 are used as the polyvinyl acetate resin to be contained in the coating fluid. If the degree of polymerization of polyvinyl acetate resin is lower than 1000, the acquired ink-accepting layer will have a weak film strength, and the ink-accepting layer may damage easily when the film is bent or scratched, or it tends to curl. Preferred degree of polymerization of the polyvinyl acetate resin is 2500 – 10,000. Examples of the polyvinyl acetate resin are polyvinyl acetate, vinyl acetate/acrylate ester copolymers, vinyl acetate/ethylene copolymers, vinyl acetate/maleate diester copolymers, vinyl acetate/acrylic acid copolymers, vinyl acetate/crotonic acid copolymers, and vinyl acetate/maleic anhydride copolymers and so on. And, commercial polyvinyl acetate resin may be used also. Examples of such resin are Goseinyl PV-500 (a product of Nippon Gosei Kagaku Kogyo K.K.), and so on. The amount of polyvinyl acetate resin in the coating fluid is 1 – 30 weight %, preferably 4 – 20 weight %, based on the total weight of the coating fluid.

[0008]
The cationic substance is added to prevent diffusion (bleeding) of the ink image and to improve chromogenicity. Preferably, the cationic substance is soluble in the organic solvent. Examples of the cationic substance are acetate salts of polyallylamines,

polyallylamines, and acrylate resins having quaternary ammonium group, and polyethyleneimines and so on. The amount of the cationic substance to be added in the coating fluid is 0.1 – 3 weight %, preferably 0.3 – 20 weight %, based on the total weight of the coating fluid. While any of the silicic anhydride obtained by dry production process and hydrated silicic acids obtained by wet production process can be used, hydrated silicic acid prpepared by wet production process is preferred in this invention. Preferred number average particle size of the synthetic amorphous silica is 1.5 – 15 μm. And, amorphous silica having a pore diameter in 100 – 200 Å range are preferred as the synthetic amorphous silica. And, amorphous silica having a specific surface area in 200 – 500 g/m^2, preferably in 300 – 400 g/m^2 range, are used. The amount of synthetic amorphous silica in the coating fluid is 2 – 35 weight %, preferably 6 – 25 weight %, based on the total weight of the coating fluid. To mix the synthetic amorphous silica in the coating fluid, a mixer such as a High Disper or Homomixer is employed to blend and disperse the silica.

[0009]

And, color pigment may be included in the ink-accepting layer to be provided on the hydrophobic supporting member of the inkjet recording material of this invention, to color the ink-accepting layer. Any of the organic and inorganic color pigments that do react with the synthetic amorphous silica can be used as the color pigment, and the color is selected based on the purpose of application. Examples of the color pigment are Fast Yellow G, Disazo Yellow, Disazo Orange, Brilliant Carmine 6B, Lake Red 4R, Phthalocyanine Green, Phthalocyanine Blue, and carbon black and so on. Amount of the color pigment in the coating fluid can be adjusted, based on the degree of coloration required by the ink-accepting layer. And, additives such as body pigment, anitoxidant, UV absorber, and/or surface active agent may be added in the coating fluid, to the extent that does not cause a damage to the property of the ink-accepting layer.

[0010]

In the inkjet recording material of this invention, the above-described coating fluid is coated and dried on a hydrophobic supporting member, to form an ink-accepting layer. As to the method of coating and drying the coating fluid on the hydrophobic supporting member to form the ink-accepting layer, it will be explained later in the explanation of the production method of the inkjet recording material of this invention. Thickness of the ink-accepting layer is 30 – 80 μm, preferably 35 – 70 μm. If the thickness of ink-accepting layer is less than 30 μm, ink absorbability may decrease and bleeding may occur easily. And, if it exceeds 80 μm, film strength may decrease. Therefore, preferably the thickness is kept within the above-said range.

[0011]

Production method of the inkjet recording material of this invention is explained next in the following. Production method of the inkjet recording material of this invention comprises coating and drying the coating fluid that contains polyvinyl acetate resin having a degree of polymerization 1000 – 10,000, and organic solvent that contains cationic substance and synthetic amorphous silica on a hydrophobic supporting member to form the ink-accepting layer. Organic solvent, polyvinyl acetate resin, cationic

substance, amorphous silica and hydrophobic supporting member being explained in the explanation of the inkjet recording material of this invention can be used here also. And, color pigment or additives being explained in the explanation of inkjet recording material of this invention can also be added in the coating fluid. Method of coating and drying the coating fluid on the hydrophobic supporting member is explained next in the following. There is no particular restriction about the method with which to coat the coating fluid, and any of the ordinary methods can be employed. For example, it can be practiced by using a bar coater, air knife coater, blade coater, roll coater, gravure coater, micro-gravure coater, fountain reverse coater, spray coater, curtain coater, E bar coater or comma coater. And, any type of drying method can be used to dry the coated fluid, as long as the drying condition does not cause thermal breakdown of the hydrophobic supporting member and can sufficiently evaporate off the organic solvent to form a film. For instance, a hot air drying oven and drying drum, etc. can be used. Thickness of the ink-accepting layer of the thus-produced inkjet recording material is 30 – 80 μm, preferably 35 – 70 μm.

[0012]
[Examples]
This invention is explained further by the following examples which, however, are not intended to limit the scope of this invention.

Examples 1 – 3 and Comparative Examples 1 – 5

Coating fluids for the ink-accepting layer having the compositions illustrated in Table 1 (Examples 1 – 3) and Table 2 (Comparative Examples 1 – 5) were coated on Mellinex 339 (thickness = 100 μm, a pure white polyester film, a product of ICI K.K.) by means of a bar coater, and then it was exposed to a stream of hot air (100°C) to dry the film, and to form an ink-accepting layer having a thickness of 40 μm (in case of Comparative Example 5, the thickness was 20 μm), and thus an inkjet recording material was prepared. In case of Example 2, a color pigment (Phthalocyanine Blue) was added to create a faint blue color in the ink-accepting layer. However, in case of Comparative Example 2, a film of ink-accepting layer was not formed.

[0013]
[Table 1]

	Example 1	Example 2	Example 3
Gosenil PV-500	10	10	10
Mizukasil P50	15		
Mizukasil P78F		15	15
Phthalocyanine Blue			0.3
Saftmer ST-3600	4.5	4.5	4.5
Methanol	10	75	75
Methylethyl ketone	90		
γ-Butyrolactone		25	25

In the table, the unit is gram (g).

[0014]
[Table 2]

	Comparative Examples				
	1	2	3	4	5
Gosenil PV-500			10		10
Gosenil M_{50}-Z_4	20				
Byron 200		10			
Mobinil 116				20	
Mizukasil P-50	15	15		15	
Mizukasil P78F			15		15
Saftmer ST-3600	4.5	4.5			4.5
Chemistat 6300H				4.8	
Methanol	10	10	75		100
Methylethyl ketone	80	90			
γ-Butyrolactone			25		33
Water				50	

In the Table, the unit is gram (g).

[0015]
Names of the products shown in the above Tables 1 and 2 represent the following.

Gosenyl PV-50 : Polyvinyl acetate resin, degree of polymerization = 5000, a product of Nippon Gosei Kagaku Kogyo K.K.
Gosenyl M_{50}-Z_4 : Polyvinyl acetate resin solution, resin content = 50%, methanol = 50%, a product of Nippon Gosei Kagaku Kogyo K.K., degree of polymerization = 500 - 800
Byron 200 : Polyester resin, a product of Toyo Boseki K.K.
Mobinil 116 : Vinylacetate resin emulsion, resin content = 50%, a product of Hechst Gosei K.K.
Mizukasil P50 : Ultra fine powder of hydrated silicic acid, average particle size = 5 μm, a product of Mizusawa Kagaku Kogyo K.K.
Mizukasil P-78F : Ultra fine powder of hydrated silicic acid, average particle size = 12.5 μm, a product of Mizusawa Kagaku Kogyo K.K.
Saftmer ST-3600 : Strongly cationic acrylic resin, resin content = 35%, containing methylcellosolve 49% and denatured alcohol 15%, a product of Mitsubishi Kagaku Kogyo K.K.
Chemistat 6300H : Cationic resin (water-soluble), resin content = about 33%, a product of Sanyo Kasei Kogyo K.K.

[0016]
These inkjet recording materials were evaluated by the following procedures described in [Standard for evaluation of inkjet recording material (1)] and [Standard for evaluation of inkjet recording material (2)]. Incidentally, no evaluation was carried out with the samples obtained in Comparative Example 2 because it did not form a film.

[0017]
[Standard for evaluation of inkjet recording material (1)]

Using a Seiko-Epson Model MJ-930C color inkjet printer (manufactured by Seiko-Epson K.K.) and an accompanying dye ink, color image was printed on the inkjet recording materials obtained in the Examples and Comparative Examples, and they were evaluated for the following test categories (1) – (7).

(1) Film strength :

Inkjet recording material printed with color image was bended, and whether a portion of the ink-accepting layer would separate or not was examined by naked eyes, and they were evaluated, based on the following evaluation standards. Results are presented in Table 3.

O : Ink-accepting layer did not peel and separate
x : A portion of the ink-accepting layer was peeled and separated

(2) Curling :

Inkjet recording material printed with color image was left on a flat surface for 1 hour, and presence or absence of curling was examined, and the results were evaluated based on the following evaluation standards. Results are presented in Table 3.

O : No curling
x : Curled

(3) Color formation :

Inkjet recording material printed with color image was examined by naked eyes, and color-forming property was evaluated based on the following evaluation standard. Results are presented in Table 3.

O : Color was fresh and clear
x : Color was not clear

[0018]

(4) Ink absorbability :

Overflow of the ink in the flat-printed area of the inkjet recording material printed with color image was examined by naked eyes, and it was evaluated based on the following evaluation standard. Results are presented in Table 3.

O : Ink did not overflow
X : Ink had overflowed

(5) Color density :

Using the color inkjet printer described above, ink of cyan color (C), ink of magenta color (M), ink of yellow color (Y), and ink of black color (BK) were flat-printed on the inkjet recording material obtained in Examples and Comparative Examples, and

optical density of the thus-obtained image was measured by using a McBeth densitometer Model TR927. Results are presented in Table 3.

(6) Color bleeding :
Using the color inkjet printer described above, two inks having different colors were printed on two nearby spots without mixing on the inkjet recording material obtained in Examples and Comparative Examples, and color bleeding was examined by naked eyes, and results were evaluated based on the following evaluation standard. Results are presented in Table 3.

O : No color bleeding
x : Significant color bleeding

(7) Color bleeding after standing :
Samples obtained in (6) but did not show color bleeding were let stand at room temperature for 1 week. After one week, color bleeding was examined by naked eyes, and results were evaluated based on the following standard.

O : No color bleeding
x : Color bleeding occurred

[0019]
[Table 3]

		Examples			Comparative Examples				
Test category		1	2	3	1	2	3	4	5
(1)		O	O	O	x	-	O	O	O
(2)		O	O	O	x	-	O	O	O
(3)		O	O	O	O	-	O	O	O
(4)		O	O	O	O	-	O	O	x
(5)	C	1.04	1.05	1.13	1.05	-	1.04	1.05	1.00
	M	0.92	0.91	1.00	0.86	-	0.92	0.90	0.91
	Y	0.77	0.78	0.78	0.74	-	0.80	0.76	0.69
	BK	1.70	1.84	1.86	1.68	-	1.74	1.70	1.69
(6)		O	O	O	O	-	O	O	x
(7)		O	O	O	O	-	x	O	-

[0020]
As clearly demonstrated by the results shown in Table 3, the inkjet recording material of this invention showed high film strength and excellent color-forming property and ink absorbability, and there was no curling nor bleeding.

[0021]
[Standard for evaluation of inkjet recording material (2)]
Using a Model RJ-1300 color inkjet printer (manufactured by Muto Kogyo K.K.) and the accompanying dye ink, image was printed on the inkjet recording material obtained in Examples and Comparative Examples, and they were evaluated for the test categories (8) – (11).

(8) Color-forming property :
Inkjet recording material printed with image was examined by naked eyes, and color forming property was evaluated based on the following evaluation standard. Results are presented in Table 4.

O : Color was fresh and clear
x : Color was not clear

(9) Color density :
Ink of cyan color (C), ink of magenta color (M), ink of yellow color (Y), and ink of black color (BK) were flat-printed, using the color inkjet printer described above, and optical density of the thus-obtained image was measured by using a McBeth densitometer Model TR927. Results are presented in Table 4.

(10) Water resistance at room temperature :
After dipping the inkjet recording material printed with image in water (room temperature) for 10 minutes, surface of the inkjet recording material was rubbed 20 times with a wet cotton, and the ink-accepting layer was examined by naked eyes and results were evaluated by the following evaluation standard. Results are presented in Table 4.

O : Absolutely no change in the ink-accepting layer
Δ : A portion of the ink-accepting layer was peeled and separated
x : Entire ink-accepting layer was peeled and separated

(11) Water resistance at 60°C :
Procedure of (1) was followed, except dipping the inkjet recording material printed with image in 60°C water for 30 minutes, to run the evaluation in a similar manner. Results are presented in Table 4.

[0022]
[Table 4]

		Examples			Comparative Examples				
Test category		1	2	3	1	2	3	4	5
(8)		O	O	O	O	-	O	O	O
(9)	C	1.10	1.19	1.29	1.08	-	1.18	1.15	1.01
	M	0.97	1.01	1.10	0.93	-	0.97	0.95	0.93
	Y	0.71	0.70	0.71	0.70	-	0.70	0.68	0.68
	BK	1.37	1.40	1.43	1.35	-	1.35	1.33	1.31
(10)		O	O	O	O	-	O	Δ	O
(11)		O	O	O	O	-	O	x	O

[0023]
As clearly demonstrated by the results shown in Table 4, the inkjet recording material of this invention excels in color-forming property and water resistance.

[0024]
[Effect of invention]
As explained comprehensively above, the inkjet recording material of this invention, has excellent water resistance, high film strength, and excellent color-forming property.

199908

Recording material for ink jet printer - has ink receiving layer, consisting of polyvinyl acetate resin, cationic substance and synthetic amorphous silica, on hydrophobic support body

Patent Assignee: FUJIREX KK (FUJI-N)

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JP 10324056 A			6			

Abstract (Basic): JP 10324056 A

NOVELTY - An organic solvent liquid containing polyvinyl acetate resin, a cationic substance and synthetic amorphous silica is applied on a hydrophobic support body. The applied liquid is then dried to form an ink receiving layer. The degree of polymerisation of polyvinyl acetate resin is 1000-10000.

USE - For ink jet printers.

ADVANTAGE - The recording material with excellent coating strength, colour development and water resistant property is obtained.

Dwg.0/0

Title Terms: RECORD; MATERIAL; INK; JET; PRINT; INK; RECEIVE; LAYER; CONSIST; POLYVINYL; ACETATE; RESIN; CATION; SUBSTANCE; SYNTHETIC; AMORPHOUS; SILICA; HYDROPHOBIC; SUPPORT; BODY

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